

Temporal Variability of Indoor Air Concentrations under Natural Conditions in a House Overlying a Dilute Chlorinated Solvent Groundwater Plume

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* Supporting Information

Current vapor intrusion (VI) pathway assessment heavily weights concentrations from infrequent (monthly–seasonal) 24 h indoor air samples. This study collected a long-term and high-frequency data set that can be used to assess indoor air sampling strategies for answering key pathway assessment questions like: “Is VI occurring?”, and “Will VI impacts exceed thresholds of concern?”. Indoor air sampling was conducted for 2.5 years at 2–4 h intervals in a house overlying a dilute chlorinated solvent plume (10–50 µg/L TCE). Indoor air concentrations varied by 3 orders of magnitude (<0.01–10 ppb, TCE) with two recurring behaviors. The VI-active behavior, which was prevalent in fall, winter, and spring involved time-varying impacts intermixed with sporadic periods of inactivity; the VI-dormant behavior, which was prevalent in the summer, involved long periods of inactivity with sporadic VI impacts. These data were used to study outcomes of three simple sparse data sampling plans; the probabilities of false-negative and false-positive decisions were dependent on the ratio of the (action level/true mean of the data), the number of exceedances needed, and the sampling strategy. The analysis also suggested a significant potential for poor characterization of long-term mean concentrations with sparse sampling plans. The results point to a need for additional dense data sets and further investigation into the robustness of possible VI assessment paradigms. As this is the first data set of its kind, it is unknown if the results are representative of other VI-sites.



INTRODUCTION

At sites where buildings overlie contaminated soils and/or groundwater, there may be a need to assess (a) whether or not the chemicals of concern are volatilizing and migrating to indoor air, and if so, (b) whether or not indoor air impacts attributable to the subsurface contamination will exceed threshold levels of concern triggering corrective action. When assessing the completeness and significance of the vapor intrusion (VI) pathway, practitioners generally follow a multiple-lines-of-evidence (MLE) approach similar to that recommended by the U.S. Environmental Protection Agency (USEPA)^{1,2} and the Interstate Technology & Regulatory Council (ITRC).³ In the MLE approach, groundwater, soil gas, and indoor air samples are collected for chemical analysis, and screening-level or more complex fate and transport model output may also be considered. Of the MLE, indoor air data tend to be heavily weighted in VI pathway decision-making. This is understandable given that the key questions above pertain to indoor air concentrations and that some decision-makers are uncomfortable with projecting indoor air concentrations from soil gas and groundwater data. Some also heavily

weight subsurface soil gas data and use it to help interpret indoor air data.⁴

With this emphasis on indoor air data, it is important to critically review whether or not conventional approaches provide adequate characterization of VI-related indoor air and potential long-term health impacts. At this time there is no definitive guidance for determining sampling frequency or duration and, based on the authors' experience, most VI pathway assessment data sets consist of results from one to four indoor air sampling events. Frequently the events are distributed across different seasons and sometimes emphasize the heating season, which is the presumed time for maximum VI impact in cold and temperate climates. The sampling usually involves the use of evacuated containers equipped with regulators set to collect indoor air over about 24 h. To date, no studies have been conducted to determine if this approach is

Received: June 3, 2013

Revised: October 22, 2013

Accepted: November 1, 2013

Published: November 1, 2013



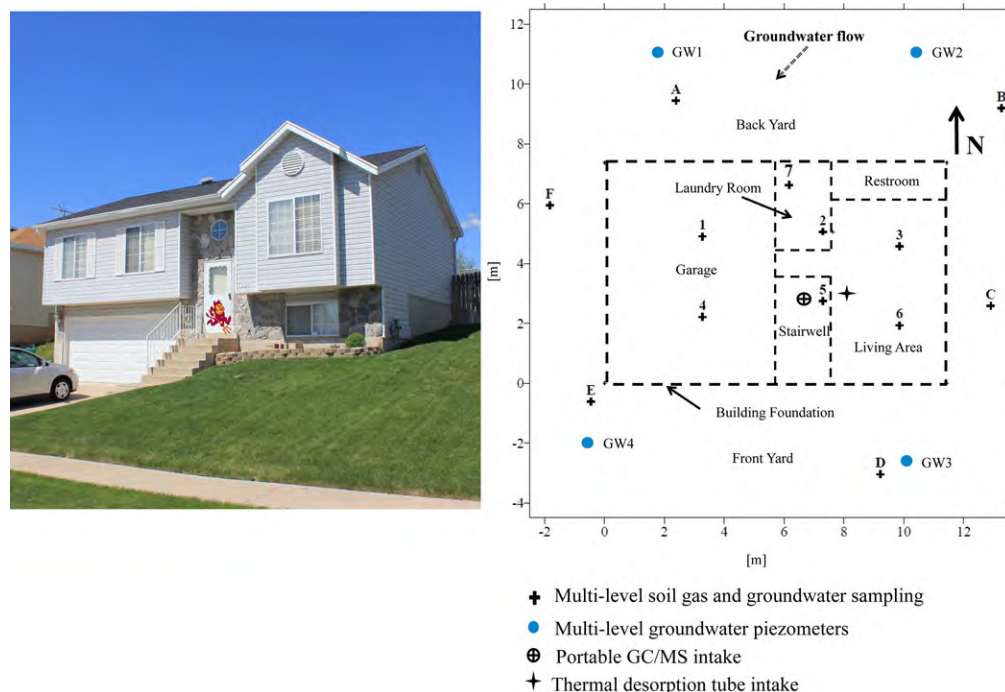


Figure 1. Photo of study house and schematic of building footprint and sampling locations.

adequate for identifying if VI is occurring, and if so, for determining if the resulting indoor air impacts are of concern.

The prediction of long-term average indoor air concentrations from short-term measurements was the interest of Hubbard et al.,⁵ who studied radon intrusion to Swedish homes. They collected daily average indoor radon concentrations over a 3.5 year period of time and observed about an order-of-magnitude variability. They used their daily average data to calculate bimonthly and annual averages, which revealed that daily concentrations could vary from about one-tenth to four times the annual average, bimonthly average results varied by about 50% above and below annual averages, and annual averages varied by about 20% across the three years of monitoring.

Similar long-term and high-frequency monitoring data sets for anthropogenic chemical VI sites have not been available. Folkes et al.⁶ report on their data from 45 unmitigated homes overlying a dissolved chlorinated solvent groundwater plume. They evaluated the temporal variability using a data set consisting of results from quarterly to semiannual collection of 24 h samples for homes with 2–10 years of data. They concluded, while the data range might span 2 orders of magnitude in concentration, individual samples were typically within about a factor of about two to three times of the annual average.

This issue was explored recently via modeling by Luo⁷ and Yao et al.⁸ Luo used a modified version of the Abreu and Johnson⁹ 3-D numerical model and a site-specific weather data

set (wind speed and barometric pressure vs time) as input to the model. A variability of two to four orders of magnitude was observed across the instantaneous indoor concentrations and about an order of magnitude variability for 24 h averages for a month-long simulation for a nondegrading chemical. Yao et al.⁸ performed simulations with a sinusoidal pressure differential input and concluded that the variability was significant and that more investigation of the temporal behavior of indoor air impacts at VI sites was warranted. Shen et al.¹⁰ modeled rainfall events and concluded that they could increase shallow soil gas concentrations in the short term and depress VI activity in the long term.

The long-term high-frequency radon data of Hubbard et al.⁵ long-term low-frequency data from Folkes et al.,⁶ and high-frequency short-term modeling results from Luo⁷ raise questions concerning the adequacy of conventional sampling approaches for VI pathway assessment. In the absence of long-term high-frequency indoor air data for some VI study sites impacted by anthropogenic chemicals, it is difficult to advance the development and validation of VI pathway assessment approaches. Thus, this study was conducted to collect a long-term high-frequency data set that can be used to assess the adequacy of VI pathway assessment schemes for identifying if VI is occurring, and if so, for determining if the resulting indoor air impacts are of concern.

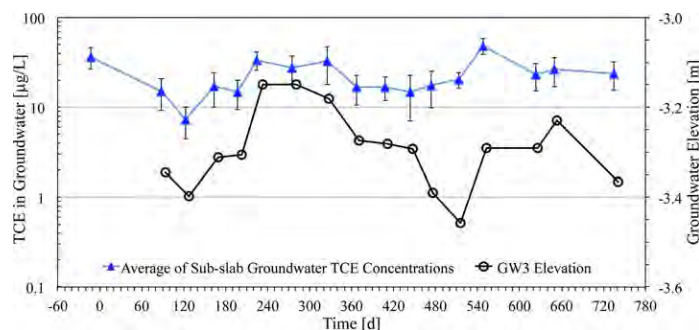


Figure 2. Monthly TCE concentrations in groundwater averaged across sampling locations beneath the foundation and monthly measured groundwater elevations at location GW3.

SITE DESCRIPTION

The study site is a split-level, two-story, three-bedroom house with a garage on the lower level in a residential community in Layton, UT. Figure 1 presents a photo of the house and its approximately 110 m² (1200 ft²) footprint. The house sits on a south-facing slope with an elevation drop of approximately 2.5 m from the back to front of the property.

Permanent multidepth soil gas and groundwater monitoring points were installed through and exterior to the house foundation at locations shown in Figure 1. Each was sealed with bentonite above and below sampling intervals and perforations through the foundation were sealed with a cement plug topped with a silicone caulk seal to ensure no connection with the subsurface. Other than shallow groundwater sampling results presented below, the data from these will be reported elsewhere.

Visual inspection of the floor and walls did not indicate any unusual construction features. Plumbing features through the foundation in the lower living space include drains in the bathroom and laundry room, with a floor drain located in the latter. Water was maintained in the P-traps in all drains during the study. There was a gap between the foundation and stem wall of about 0.6 cm wide × 180 cm long observed beneath the stairwell connecting the upper and lower living spaces.

The house overlies a regional dilute groundwater plume containing 1,1-dichloroethene (1,1-DCE), 1,1,1-trichloroethane (1,1,1-TCA), and trichloroethylene (TCE), with regional flow to the southwest. Groundwater is estimated to be about 2.5 m (8.3 ft) below the house slab (BS), based on absence of water in the 1.8 m (6 ft) subslab sampling points and the presence of water in the 2.7 m (9 ft) subslab sampling points. The average of dissolved TCE concentrations in groundwater in samples collected beneath the foundation ranged from about 10–50 µg/L over 2.5 years as shown in Figure 2. The mean of the average subslab groundwater concentrations was 23 ± 10 µg/L over the study period.

The soil beneath the house consists predominantly of fine sandy silt with fine sand stringers. The soil moisture adjacent to the house, based on three soil cores collected in late spring, is 0.20 ± 0.02 g-H₂O/g-soil within 0.6 m (2 ft) of ground surface and then increases and is relatively consistent with depth at 0.25 ± 0.01 g-H₂O/g-soil to 3.7 m (12 ft) below ground surface. For reference, 0.20 g-H₂O/g-soil is equivalent to 80% water saturation assuming that 0.25 g-H₂O/g-soil represents

fully saturated soil. Depth to water in the shallowest screen interval of the four exterior multilevel groundwater piezometers is about 3.3 m, which suggests complex hydraulics through the sand stringer network. The depth to groundwater varied with time by ± 0.27 m (0.9 ft) about the time-averaged depth to groundwater in the shallowest exterior piezometers; sample data from GW-3 are presented in Figure 2.

Outdoor temperatures ranged from -15 to $+38$ °C for the duration of the study. The average wind speed was 1.1 m/s with gusts up to 11.5 m/s and a dominant southerly direction. The average annual rainfall at the site was about 50 cm, with most of it occurring around late spring and early summer. The lawn was watered by an automatic sprinkler system during the late spring through early fall months.

Indoor temperature was maintained at approximately 20.5 °C with a central forced-air heating/cooling system. Furniture, with the exception of a few tables and chairs, was removed. Visual inspections were conducted, activity logs were recorded, and indoor air data were reviewed to ensure that indoor sources of the chemicals of interest were not present. No one lived in the house during the study, but there was study-related activity in and around the house approximately 20% of time.

The indoor air exchange rate [1/d] in the lower level was characterized starting in late December 2011 ($t = 120$ days on all plots) by continuous indoor release (5 mL/min) and monitoring of sulfur hexafluoride (SF₆) on 30 min intervals. The building exchange flow rate was calculated as $(1 \times 10^9 / \text{SF}_6 \text{ concentration [ppbv]}) \times 5 \text{ mL/min}$, and the exchange rate was calculated as (building exchange flow rate/effective air exchange volume). Concentrations measured during the transient period following a step increase in SF₆ release rate were used to determine the effective air exchange volume (350 m³). Instantaneous and daily averaged exchange rates are presented in Figure 3. As can be seen, the exchange rate varied seasonally. It was largest and had greatest short-term variability in the fall to spring months (typically 15–25 d⁻¹ daily averages, with instantaneous excursions across the 10–35 d⁻¹ range), and smaller and less variable in the summer months (typically 5–10 d⁻¹ daily averages, with instantaneous excursions across the 4–12 d⁻¹ range). The measured range of daily averaged exchange rates is similar to results reported in the literature for occupied homes.¹¹

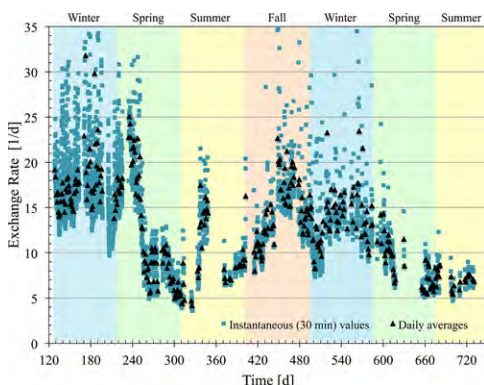


Figure 3. Instantaneous and daily average indoor air exchange rate for the lower level of the study house.

EXPERIMENTAL METHODS

Real-time sampling focused on indoor air concentrations in the lower level of the house at locations shown in Figure 1. It was conducted using two methods: (a) near-instantaneous 1 min 100 mL samples collected every 2 h and analyzed using a field-portable gas chromatography/mass spectroscopy (GC/MS) instrument (HAPSITE, Inficon, Syracuse, NY), and (b) time-averaged 12 L samples collected over 4 h on sorbent tubes and later analyzed by thermal desorption and GC/MS.

With the HAPSITE instrument, a 100 mL sample collection purge was conducted prior to drawing a second 100 mL sample through a heated probe and onto an internal tribed sorbent trap. Sorbed chemicals were subsequently desorbed using a ramped temperature program (55 °C hold for 80 s followed by a 30 °C/min ramp to 110 °C) and analyzed by GC/MS using selected ion monitoring (SIM) mode. The total time for sample collection and analysis was approximately 6 min with a method detection limit (MDL) of 0.06 ppb, for TCE. Calibration and quality control procedures followed protocols discussed by Gorder and Dettenmaier.¹²

Sorbent tube samples were collected using two customized SRI Instruments (SRI Instruments, Torrance, CA) 20-stream gas sampling valves, a vacuum pump (Rena 301 series, model BE-3012 vacuum/pressure pump), and a vacuum-configured, 0–100 mL/min mass flow controller (Alicat Scientific, Tucson, AZ). An SRI Instruments 6-channel data system driven by SRI PeakSimple software was used to sequence sample collection and maintain sampling flow at 50 mL/min. Multibed sorbent tubes (0.64 × 15.2 cm-long) were packed with Tenax-GR and Carboxen-569 and fitted with Markes DiffLok caps (Markes International, UK) for tube/sample preservation. As configured, 38 4-h samples were collected every 6.3 days. Sampling tubes were unloaded from the autosampler, sealed with Swagelok brass caps with Teflon ferrules, and packed for express shipment to an analytical laboratory at Arizona State University (ASU) for analysis. The next set of conditioned tubes was then added to the autosampler.

Sorbent tubes were analyzed using a Markes Ultra autosampler and Markes Unity thermal desorber (Markes International, UK) connected to an HP5890 gas chromatograph equipped with a Restek 60 m Rxi-5 capillary column and an HP5972 mass spectrometer. Samples were analyzed using

SIM mode with an MDL of 0.008 ppb. Quality assurance/quality control (QA/QC) activities included calibration, continuous calibration verification, blanks, trip blanks, trip spikes, and internal standards. The calibration curve fitting consistently gave R^2 regression over 0.99, blanks and trip blanks showed nondetect for the target chemicals, and internal standard recovery was consistently above 96%.

The field-portable GC/MS was the only sampling system for about the first 9 months of this study. For the next 12 months, concentrations were measured by both methods. In the latter portion of the study, the concentrations come mostly from the sorbent tube sampling as the field-portable instrument was frequently unavailable or inoperative. It should be noted that the two approaches sampled air at two different lower-level locations as shown in Figure 1. The field-portable GC/MS sampled air in the stairwell while the sorbent tubes sampled air in the adjoining living space. Thus, the field-portable GC/MS intake was located in closer proximity to the suspected vapor intrusion point (the foundation-wall gap) than the sorbent tube sampling input, and the observed temporal variability in indoor concentrations represents only the lower level air space.

As discussed above, the indoor air exchange rate was determined by SF_6 tracer release and monitoring. SF_6 concentrations were determined using an autosampling GC in combination with a pulse-discharge detector (PDD).

This study also included high frequency monitoring of indoor and outdoor temperatures, indoor-outdoor and subsurface-indoor pressure differentials, barometric pressure, wind speed and direction, precipitation and synoptic snapshots of soil gas and groundwater concentrations. Those data and their analyses, including evaluation of subsurface temporal variability and correlations between environmental factors and indoor air concentrations will be reported elsewhere.

RESULTS AND DISCUSSION

Indoor Air Concentrations. TCE concentrations are presented and discussed as their behavior is representative of the suite of chlorinated compounds monitored in indoor air at the study house.

Figure 4 presents results from February 2010 to August 2012, with time (t) = 0 being 8:00 AM on 08/15/2010; this time was selected as it was when the first synoptic sampling of

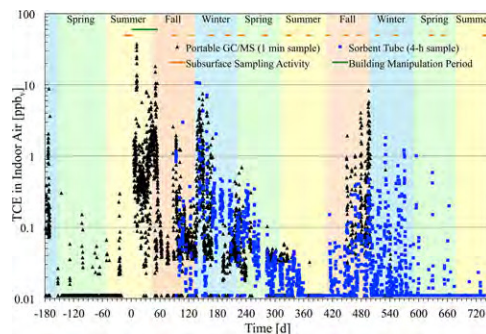


Figure 4. Indoor air TCE concentrations measured by portable GC/MS and sorbent tubes from February 2010 to August 2012 (note: values ≤ 0.011 ppb, are plotted as 0.011 ppb, to make it clear that samples were collected at those times).

the multilevel soil gas and groundwater installations occurred. For the 4 h average sorbent tube samples, analytical results <0.011 ppb, are plotted as 0.011 ppb, in this figure to make it clear that samples were collected at those times (the data markers would not appear otherwise with a 0.01 ppb, lower graph limit). Instantaneous concentrations measured with the portable GC/MS instrument were not censored at its 0.06 ppb, MDL; instead, values >0.011 ppb, are plotted as quantified and results <0.011 ppb, are plotted as 0.011 ppb, as for the sorbent tube sample results. As discussed in U.S. Geological Survey,¹³ the USEPA MDL determination approach emphasizes minimization of false-positives using statistical analysis of detector response, and there is value and justification to presenting results $<MDL$ when data-rich analyses (e.g., GC/MS/SIM) are used to determine concentrations. In this case, data in the 0.01 – 0.06 ppb, range are presented as they help discern temporal trends in indoor air concentrations; however, it should be noted that these data are qualified as being less than the MDL for that instrument.

There were periods from $2 < t < 40$ days and $47 < t < 54$ days, when indoor pressures were manipulated to create under-pressurized conditions for other studies conducted at the house. One of those studies inadvertently introduced a TCE indoor air source that was identified and removed at $t = 54$ days. These periods are identified and those data are shown in Figure 4, but the results were removed from the data set in the analyses and assessment of indoor air sampling approaches discussed below. Also indicated in Figure 4 are time intervals when synoptic soil gas and groundwater sampling were conducted; those results are being used to study the transient behavior of subsurface chemical distributions beneath and surrounding the house, and will be reported elsewhere.

Ignoring the $t = 0$ – 60 day time period, TCE concentrations in indoor air varied by about two to three orders-of-magnitude (<0.01 to 10 ppb_v). Given that changes in the air exchange rate are less than an order of magnitude, the indoor air concentration changes must reflect changes in TCE mass entry rate to the house. Embedded within the 2.5 year sampling history are two recurring VI behaviors. There are “active” VI periods, which are prevalent in fall, winter, and sometimes into early spring, that involve varying levels of VI impacts intermixed with sporadic periods of nondetect concentrations. Figure 5 presents data from a representative VI-active period occurring during winter months. For this sample VI-active period, TCE

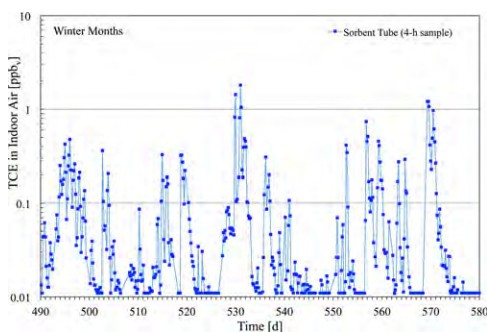


Figure 5. Temporal behavior of TCE in indoor air during a VI-active period (values ≤ 0.011 ppb_v are plotted as 0.011 ppb_v).

concentrations increase and then decrease over multiday time periods, with maximum concentrations ranging from about 0.5 – 2 ppb_v. One- to four-day periods of nondetect concentrations (<0.01 ppb_v) are interspersed throughout the VI-active periods.

There also are inactive, VI-dormant periods, which are prevalent in late spring and summer; these involve mostly nondetect indoor air concentrations and sporadic one- to two-day periods of VI-activity. Figure 6 presents data from a

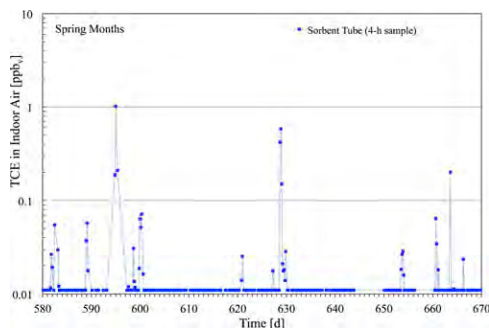


Figure 6. Temporal behavior of TCE in indoor air during a VI-dormant period (values ≤ 0.011 ppb_v are plotted as 0.011 ppb_v).

representative VI-dormant period occurring during summer months. For this sample VI-dormant period, there are one- to three-week periods of nondetect concentrations and brief increases in indoor concentrations to levels (0.05 – 1.0 ppb_v) similar to those observed during the VI-active period.

Implications for VI Pathway Assessment–Synthetic 24 h Average Concentration Data Set and Simple Sampling Schemes. The data presented here comprise the longest and highest-frequency monitoring record to date for anthropogenic chemical impacts to indoor air at a vapor intrusion site. Thus, it is unknown whether or not the data are representative of other VI-sites, and one must be cautious in extending lessons-learned below to other VI sites. Nevertheless, the data provide the first opportunity to evaluate whether or not conventional sampling approaches are likely to yield correct answers at this and any similar sites to the two primary VI-pathway assessment questions:¹ (a) is the VI pathway complete at a site (e.g., are there indoor air impacts that are attributable to VI activity)?, and (b) does the potential exposure to VI-related indoor air impacts exceed target exposure thresholds?

The frequency and duration of indoor air sampling used in this study are not practicable for routine VI pathway assessment. For the past decade, 24 h samples have been the standard for VI-pathway assessment; although longer-term (one- to three-week) passive sorbent sampling is well validated,¹⁴ it is not commonly used in the U.S. The data in Figure 4, therefore, were converted to a synthetic 24 h daily average concentration data set. This approach is similar in principle to the radon data analysis of Hubbard et al.,⁵ where higher-frequency (daily) data were converted to longer-term (bimonthly and annual) average concentrations to assess the utility of longer sampling periods for exposure assessment.

The following procedure was used to create the synthetic 24 h data set presented in Figure 7: (i) $0 < t < 60$ day data were

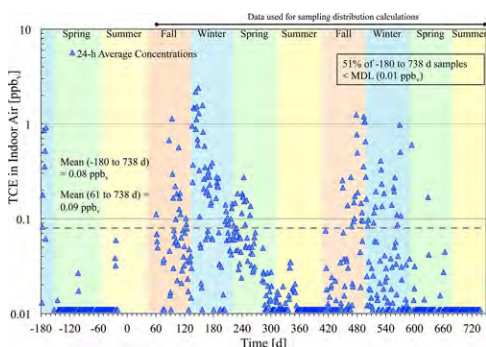


Figure 7. Synthetic 24 h sample data set derived from data in Figure 4 (excluding $0 \leq t \leq 60$ day data; values ≤ 0.011 ppb, are plotted as 0.011 ppb).

removed as discussed above; (ii) 24 h average concentrations were calculated separately for the portable GC/MS and sorbent tube data sets; and (iii) the two daily average data sets were combined by averaging when two 24 h average values were available for the same day, or the single value was used when only one concentration value was available. A seasonal comparison of the 24 h average concentration distributions is provided in Supporting Information Figure S1. All 24 h average concentrations were calculated for 8 a.m. to 8 a.m. sampling periods and the value assigned to the midpoint time (8 p.m.) for plotting purposes. Synthetic concentrations were only calculated when actual monitoring results were available for at least 8 h of a 24 h period. To fully emulate the features of a real data set, a method detection limit was defined and used to truncate the synthetic data set at 0.01 ppb. Whenever the procedure above produced a 24 h concentration $< \text{MDL}$ then that concentration was assigned a value of one-half the MDL (0.005 ppb) as is sometimes done in practice when manipulating VI data sets. Results < 0.011 ppb, are plotted as 0.011 ppb, in Figure 7 for consistency with other figures.

The resulting synthetic data set is plotted in Figure 7. There are 723 24-h average concentrations distributed across 858 days (84% coverage, excluding $0 < t < 60$ days). The mean and median concentrations for the synthetic data set are 0.08 and < 0.01 (0.009) ppb, respectively. As can be seen the 24 h average values represent the overall trends seen in Figure 4, with similar seasonal variability and VI-active fall-summer-spring and VI-dormant summer seasons. The peak concentration (2.4 ppb) is about 20% lower than in the actual shorter sampling interval data set due to the time-averaging, so concentrations vary by about 2 orders of magnitude above the 0.01 ppb, MDL. There is a high percentage of values at or near the MDL; for example, 51% are less than or equal to the MDL and 64% are less than or equal to twice the MDL.

Given the characteristics of the data set (two-order-of-magnitude range and a high frequency of nondetects), one might wonder about the outcomes from conventional VI sampling approaches. To examine this, the data subset from $61 < t < 738$ days, which spans eight seasons, was used to generate outcomes for three simple sampling plans. The mean concentration for that time interval is 0.09 ppb, the maximum value is 2.4 ppb, and 44% of the concentrations values are less than or equal to the 0.01 ppb, MDL.

The three simple indoor air sampling plans involve collecting (a) one sample per season (fall/winter/spring/summer) over one year, (b) collecting one sample in summer and one in winter, and (c) collecting two samples in winter. The intent here is not to explore all possible sampling plans or determine optimal plans, although that topic is currently being explored with the data set and will be reported elsewhere. The goal is to examine the results from three plans that are not atypical of current practice to get a sense of the possible outcomes from sparse and infrequent sampling.

Each sampling plan was simulated 5000 times to develop representative statistics. For a given realization, each seasonal sample was randomly collected from the distribution of all concentrations for that season. For example, all values in the two winter seasons shown in Figure 7 were combined into one winter concentration distribution, and samples were pulled randomly from that distribution in each realization. Basic statistics (mean, median, quartiles) for the distributions of sampled concentrations from the 5000 realizations were compared with the statistics of the original distributions to ensure consistency.

The seasonal concentration distributions that were sampled are presented in Figure 8, along with the aggregate $t = 61$ to

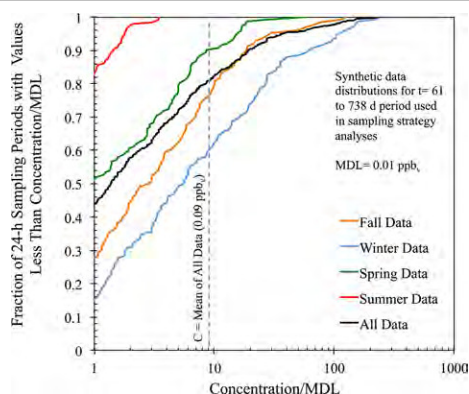


Figure 8. Seasonal and all indoor air concentration distributions derived from the $t = 61$ –738 day synthetic data in Figure 7, with concentrations normalized to the MDL assigned to the synthetic data set (0.01 ppb).

738 day data distribution. Concentrations in this figure are normalized to the MDL as that is often an important reference in reviewing data. For example, results close to the MDL are often considered in practice to be the result of analytical variability rather than subsurface VI impacts. The MDL may be regarded as a reference for VI signal strength; it is much easier to decide if VI is occurring when all sample results are much greater than the MDL than if they are close to the MDL. As can be seen, there are fewer values $\leq \text{MDL}$ (concentration/MDL ≤ 1) and more higher concentration values (concentration/MDL ≥ 10) as one moves from summer to spring to fall to winter. The percentage of concentrations less than the mean is $> 50\%$ for all seasons, increasing from winter to fall to spring to summer, with 100% of all summer concentrations being less than about 40% of the mean.

Table 1. Probability of One or More Indoor Air Samples Exceeding the Target Concentration for a Range of (Target Concentration/True Mean Concentration) Ratios and Three Different Sampling Strategies^a

(target/mean) concentration × ratio		sampling strategies							
		fall, winter, spring, and summer sampling (four samples total)				winter and summer sampling (two samples total)		two winter samples (two samples total)	
		number of samples exceeding the target concentration							
		1	2	3	4	1	2	1	2
0.2		94%	64%	20%	1%	72%	4%	91%	51%
0.5		80%	34%	5%	0%	54%	0%	80%	28%
1		60%	14%	1%	0%	41%	0%	66%	15%
2		38%	4%	0%	0%	28%	0%	49%	9%
5		17%	1%	0%	0%	12%	0%	22%	1%
10		10%	1%	0%	0%	8%	0%	16%	1%

^aTrue Mean = 0.09 ppb, for the synthetic data set. MDL = 0.01 ppb, for the synthetic data set.

Probability of False Negative and Positive Results When Comparing Sparse Sampling to Action Levels. In practice, sampling results are compared against regulatory action levels, and exceedances trigger follow-on actions (e.g., additional sampling, mitigation). The synthetic data were used to study outcomes from sparse sampling using hypothetical action levels normalized to the true mean concentration for the data set, using action levels less than, equal to, and greater than the mean (action level/mean concentration = 0.2, 0.5, 1.0, 2, 5, 10). The results are presented in Table 1 as probabilities of one or more samples exceeding the different action levels.

Typically the action level represents a long-term average concentration that is deemed protective; however, it might also represent a threshold for acceptable short-term exposures. For the former, we are concerned with (a) probabilities of one or more samples not exceeding the threshold when the true mean \geq threshold (false negative condition), and (b) probabilities of one or more samples exceeding the threshold when the true mean $<$ threshold (false positive condition). Table 1 shows that the probability of false negative conclusions ($=100\% -$ values in Table 1) is as low as 6% and increases to 40% as the ratio of (action level/true mean) approaches unity and one exceedance is enough to trigger action; the probability also increases significantly as the number of sample exceedances required increases. The probability of false positives is at least 10% and increases to about 40% as the ratio of (action level/true mean) approaches unity and one exceedance is enough to trigger action; the probability also decreases significantly as the number of sample exceedances required increases. There are differences between the three sampling plans, with the four season and winter-only sampling plans having the lowest false negative and highest false positive percentages.

For cases where the action level represents a threshold for acceptable 24 h exposures, we are concerned with probabilities of samples not exceeding the action level when the true maximum concentration \geq action level (false negative condition). For this synthetic data set, the probability of false negative decisions ($=100\% -$ values in Table 1) exceeds about 80% when the (action level/true mean) > 5 . As the true maximum concentration $>10\times$ true mean for this data set, there is no chance of a false positive condition.

Probability of Under- and Overestimating the Long-Term Mean Concentration Using Sparse and Infrequent Sampling. The mean of indoor air sample concentrations is a relevant statistical quantity for exposure considerations. Figure 9 presents the distributions of mean concentrations calculated

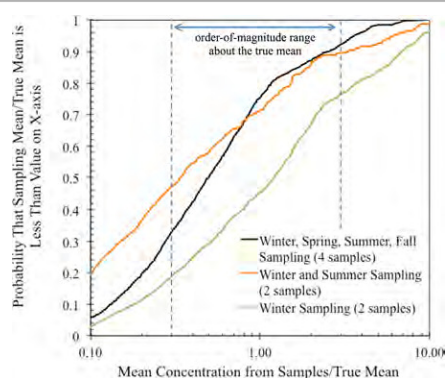


Figure 9. Distribution of sample means for 5000 sampling realizations and three simple sampling schemes, with concentrations normalized by the true mean for the $t = 61\text{--}738$ day synthetic data (0.09 ppb,) shown in Figure 7

from samples for the three sampling plans, using the 5000 sampling realizations. Results are normalized to the true mean for the data set. Vertical lines that bracket an order of magnitude range about the true mean are drawn on the plot (mean of samples/true mean = 0.3 and 3.0). As can be seen, there is about a 32% probability that four-season sampling will produce a mean concentration that is $\leq 30\%$ of the true mean and a smaller 8% probability that the sampling mean will be greater than three times the true mean. For the winter and summer sampling plan, there is about a 48% probability of producing a mean concentration that is $\leq 30\%$ of the true mean and a smaller 11% probability that the sampling mean will be greater than three times the true mean. For the two winter samples plan, there is about an 18% probability of yielding a mean concentration that is $\leq 30\%$ of the true mean and a slightly larger 22% probability that the sampling mean will be greater than three times the true mean. There is about a 60% probability that the sampling mean will be within the order-of-magnitude range about the true mean for the four-season sampling plan, a 41% probability that the sampling mean will be within the order-of-magnitude range about the true mean for the winter/summer sampling plan, and a 60% probability that the sampling mean will be within the order-of-magnitude range about the true mean for the two winter samples plan.

Future Needs for Robust VI Pathway Assessment Paradigm Development. The results above suggest a need for discussion and linking of sampling schemes and decision rubrics in creation of future VI assessment paradigms, and examination of possible outcomes for sites with dense data sets. Use of the three simple sampling schemes illustrates that there can be relatively high probabilities of false-negative decisions and poor characterization of long-term mean concentrations with sparse data sets typical of current practice. As this is the first long-term and high-frequency data set for VI impacts from anthropogenic chemicals, similar data sets from other sites are needed to test the robustness of possible VI pathway assessment paradigms. As mentioned above, it is unknown whether or not the data from this study site are representative of other VI-sites, so caution should be exercised in extending lessons-learned at this site to other VI sites.

ASSOCIATED CONTENT

* Supporting Information

Population Distributions of the 24 h average concentrations from the portable GC/MS and sorbent tube data sets are provided in Figures S1 and S2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the U.S. Department of Defense, through the Strategic Environmental Research and Development Program (SERDP).

REFERENCES

- (1) U.S. Environmental Protection Agency. OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance); U.S. Environmental Protection Agency: Washington, DC, 2002.
- (2) U.S. Environmental Protection Agency. Superfund Vapor Intrusion FAQs; U.S. Environmental Protection Agency: Washington, DC, 2012.
- (3) Interstate Technology & Regulatory Council. Vapor Intrusion Pathway: A Practical Guideline; Interstate Technology & Regulatory Council: Washington, DC, 2007.
- (4) New York State Department of Health. Guidance for Evaluating Soil Vapor Intrusion in the State of New York; NY State Department of Health: Troy, NY, 2006.
- (5) Hubbard, L. M.; Mellander, H.; Svedejemark, G. A. Studies on temporal variations of radon in Swedish single-family houses. *Environ. Int.* 1995, 22, S715–S722.
- (6) Folkes, D.; Wertz, W.; Kurtz, J.; Kuehster, T. Observed spatial and temporal distributions of CVOCs at Colorado and New York vapor intrusion sites. *Ground Water Monit. Rem.* 2009, 29, 70–80.
- (7) Luo, H. Field and modeling studies of soil gas migration into buildings at petroleum hydrocarbon impacted sites. Ph.D. Dissertation, Arizona State University, Tempe, AZ, 2009.
- (8) Yao, Y.; Pennell, K. G.; Suuberg, E. M. The influence of transient processes on vapor intrusion processes. Paper for the AWMA Vapor Intrusion Conference, September 2010.
- (9) Abreu, L.; Johnson, P. C. Effect of vapor source-building separation and building construction on soil vapor intrusion as studied with a three-dimensional numerical model. *Environ. Sci. Technol.* 2005, 39 (12), 4550–4561.
- (10) Shen, R.; Pennell, K. G.; Suuberg, E. M. A numerical investigation of vapor intrusion: The dynamic response of contaminant vapors to rainfall events. *Sci. Total Environ.* 2012, 437, 110–120.
- (11) Yamamoto, N.; Shendall, D. G.; Winer, A. M.; Zhang, J. Residential air exchange rates in three major US metropolitan areas: Results from the relationship among indoor, outdoor, and personal air study 1999–2001. *Indoor Air.* 2009, 20, 85–90.
- (12) Gorder, K. A.; Dettenmaier, E. M. Portable GC/MS methods to evaluate sources of cVOC contamination in indoor air. *Groundwater Monit. Rem.* 2011, 31 (4), 116–119.
- (13) U.S. Geological Survey. New Reporting Procedures Based on Long-Term Method Detection Levels and Some Considerations for Interpretations of Water-Quality Data Provided by the U.S. Geological Survey National Water Quality Laboratory; U.S. Geological Survey: Reston, VA, 1999.
- (14) U.S. Environmental Protection Agency. Fluctuation of Indoor Radon and VOC Concentrations Due to Seasonal Variations; U.S. Environmental Protection Agency: Washington, DC, 2012.